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Plasmonic Paper as a Highly Efficient SERS Substrate

by Chang H. Lee, Mikella E. Hankus, Limei Tian, Paul M. Pellegrino, and Srikanth Singamaneni

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Chang H. Lee, Limei Tian, and Srikanth Singamaneni
Department of Mechanical Engineering and Materials Science
Washington University, St. Louis, MO 63130

Mikella E. Hankus and Paul M. Pellegrino
Sensors and Electron Devices Directorate, ARL

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We report a novel surface enhanced Raman Scattering (SERS) substrate platform based on a common filter paper adsorbed with plasmonic nanostructures. Paper based SERS substrate overcomes many of the challenges associated with conventional SERS substrates based on rigid substrates such as silicon and glass. The paper-based design results in a substrate that combines all of the advantages of conventional rigid and planar SERS substrates in a dynamic flexible scaffolding format. We discuss the fabrication, physical characterization and SERS activity of our novel substrates using non-resonant analytes.

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Plasmonic paper as a highly efficient SERS substrate

Chang H. Lee[1], Mikella E. Hankus[2], Limei Tian[1], Paul M. Pellegrino[2*] and Srikanth Singamaneni[1 *]

[1] Department of Mechanical Engineering and Materials Science, Washington University, St. Louis, MO 63130

[2] U.S. Army Research Laboratory, Sensors and Electron Devices Directorate, Adelphi, MD 20783-1197

ABSTRACT

We report a novel surface enhanced Raman Scattering (SERS) substrate platform based on a common filter paper adsorbed with plasmonic nanostructures. Paper based SERS substrate overcomes many of the challenges associated with conventional SERS substrates based on rigid substrates such as silicon and glass. The paper-based design results in a substrate that combines all of the advantages of conventional rigid and planar SERS substrates in a dynamic flexible scaffolding format. We discuss the fabrication, physical characterization and SERS activity of our novel substrates using non-resonant analytes.

Keywords: surface enhanced Raman Scattering (SERS), paper substrate, plasmonic nanostrucutres

INTRODUCTION

Surface enhanced Raman scattering (SERS) is rapidly emerging as a powerful technique for the trace level detection of various biological and chemical species and is believed to make a huge impact in life sciences, environmental monitoring, and homeland security.[1,2,3,4,5,6,7] Numerous SERS substrates from roughened noble metal surfaces to e-beam patterned metal nanostructures with enhancement factors ranging from 10^4 to 10^{10} have been demonstrated over the last two decades.[6,8,9,10,11] Very high enhancement factors ($> 10^9$) have been reported for SERS substrates fabricated from top-down and bottom-up approaches such as e-beam lithography, colloidal lithography, on-wire lithography and self- and directed-assembly, which enable precise control over the size, shape, and organization of the metal nanostructures.[12,13,14,15,16] On the other hand, 3D SERS substrates such as photonic crystal fibers and porous alumina membranes decorated with nanoparticles and periodic nanohole arrays also offer large SERS enhancements (10^6 - 10^9) owing to the large surface area within the source laser footprint and efficient light-matter interaction compared to the 2D counterparts.[17,18,19,20]

Although most of these studies clearly demonstrate that SERS substrates hosting closely separated metal nanostructures and/or sharp tips result in large enhancements, an important practical consideration apart from the cost, which is often overlooked, is the ease and efficiency of the sample collection. In real-world applications such as explosive detection,

the efficiency of sample collection becomes a decisive factor. For example, in the case of explosives such as trinitrotoluene (TNT), which inherently have low vapor pressure (~10 ppb$_v$ at room temperature), intentional packaging further lowers the actual vapor concentration by more than an order of magnitude.[21] For detection of such explosives, it is extremely important to collect particulates (few μg), that are invariably present on the surface of objects exposed to the explosive. Physical swabbing, puffer systems (aerodynamic), and direct vapor sniffing are recognized as efficient methods to collect trace amounts of analytes. In particular, swabbing the surface under investigation with a soft and flexible substrate (swab) is a highly practical and efficient method to maximize the sample collection from a real-world surface. In fact, this strategy is being extensively employed for passenger screening at airports using ion mobility spectroscopy.[22] On the contrary, conventional SERS substrates based on silicon, glass, and porous alumina, which are conceived for homeland security applications, are not compatible with such efficient sample collection process due to their non-conformal, rigid and brittle nature.

Considering the many issues still associated with SERS substrates, there is a need for a sensitive, cost-efficient, reproducible, uniform, and flexible substrate. Such a substrate would have applications not only to first responders and military personal but also to several areas of medical, food analysis, and environmental research. We and others have introduced a new SERS substrate platform that overcomes many of the challenges associated with typical previous SERS substrates.[23,24,25] Our novel SERS platform consists of plasmonic nanostructures adsorbed on flexible filter paper-based scaffolding. Our paper-based scaffolding results in a substrate that combines all of the advantages of a FON in a flexible scaffolding format. Our substrate is thus cost-efficient, highly sensitive, robust, amiable to several different environments and target analytes. Paper SERS substrates exhibit high sensitivity (0.5 nM BPE) and excellent reproducibility (~ 15% RSD). We demonstrate the detection of less than 140 pg of 1,4-benzenedithiol (1,4-BDT) residue spread over 4 cm^2 surface by simply swabbing the AuNR loaded paper on the surface.

RESULTS AND DISCUSSION

Gold nanorods were employed as SERS media owing to the facile synthesis and tunability of the localized surface plasmon resonance with aspect ratio. Nanorods with ~ 60 nm length and ~18 nm diameter (aspect ratio approximately 3.3) were synthesized using seed-mediated approach. (Figure 1A). UV-Vis extinction spectra of the gold nanorod solution showed the two characteristic peaks at ~ 515 nm and 740 nm corresponding to the transverse and longitudinal plasmon resonances of gold nanorods, respectively (Figure 1B).[26] Extinction spectrum obtained from the filter paper adsorbed with gold nanorods showed the transverse and longitudinal plasmon blue shifted compared to the gold nanorod solution. The observed blue shift can be attributed to the change in the dielectric ambient (from water to air/substrate) with an effective decrease in the refractive index. The blue shift of the longitudinal plasmon peak (~45 nm) was larger than that of the transverse band (~5 nm), due to the higher refractive index sensitivity of the longitudinal plasmon resonance compared to the transverse band.[27]

The paper scaffolding used in this study was a common laboratory filter paper (Whatman #1). The choice of the paper substrate is based on the fact that filter paper chosen is almost completely comprised of α-cellulose (98%) and ensures

minimal interference from other components (trace elements, coatings etc.).[28] Figure 1A shows the hierarchical fibrous morphology of the filter paper from SEM and AFM. The paper largely consisted of micro scale (~ 10 μm) cellulose fibrous strands interwoven together. Smaller microfibers (average diameter of ~ 0.4 μm) made part of the large fibrous structure with nanofibers braided in between. The RMS surface roughness of the paper was 72 nm scanned over 5×5 μm^2 area, indicating that the paper had a large surface area. Paper has gained much interest in recent years as a low-cost and ideal platform for building portable miniature diagnostic devices suitable for developing countries, resource-limited environments, and point-of-care.[29,30] Paper is a versatile and common material that finds many uses in consumer oriented products because its source (cellulose) is abundant in nature, renewable, inexpensively produced and recycled.[31] Paper is also biodegradable, biocompatible, and has ability to easily wick and absorb fluids.[32] Recently, there have been extensive efforts to develop low-cost potable biomedical diagnostic devices by printing microfluidic patterns on paper, which create hydrophobic barriers that define channels and reaction zones to fabricate an analytical system.[33]

SEM images revealed uniform and dense adsorption of the gold nanorods on the surface without any signs of large scale aggregation (Figure 1B). Low magnification SEM image shows uniform speckled surface morphology of the paper indicating highly uniform adsorption. Despite the inherent heterogeneity of the paper morphology (pores and fibers of different sizes), the adsorption of the nanorods was found to be highly uniform (Figure 1B). Higher magnification image shows the nanorods decorating the micro and nanofibers of the paper surface (inset of Figure 1B). The number density of the gold nanorods on the filter paper was $98 \pm 22 / \mu m^2$, determined from a number of AFM images (not shown). Uniform and high density adsorption of CTAB (cationic surfactant) capped gold nanorods to polymer surfaces can be a significant challenge.[34,35] However, we observed that once the gold nanorods were adsorbed on the filter paper, even vigorous rinsing with water or alcohol did not noticeably alter the gold nanorod density, suggesting the stability of the paper SERS substrate for deployment in liquid environments. Cellulose has a large number of hydroxyl groups, which are accessible for attaching positively charged species.[36,37] The uniform, irreversible, and high density adsorption of the gold nanorods is possibly due to the electrostatic interaction between the positive charged nanorods and the filter paper.

Autofluorescence can be a significant problem when using paper as substrate in an optical analysis. Fluorescence images of filter paper revealed strong green (525 nm) fluorescence emission (Figure 2A-D). On the other hand, in the case of filter paper adsorbed with gold nanorods, autofluorescence of the filter paper was significantly quenched due possibly to non-radiative energy transfer.[38,39] Fluorescence spectra shows that the filter paper adsorbed with gold nanorods has virtually no fluorescence and this feature is of a great advantage in using paper as a SERS substrate as the unwanted autofluorescence is self-subdued (Figure 2B). Also for SERS using gold nanorods, 785 nm wavelength laser is typically used to place the longitudinal band of a gold naorod between the wavelengths of the excitation source laser and vibrational band of interest to optimize SERS enhancement.[40] This laser wavelength, which is far from the fluorescence excitation wavelength, also ensures weak autofluorescence.

Trans-1,2-bis(4-pyridyl)ethene (BPE) was employed as a non-resonant analyte for investigating the efficiency of the paper based SERS substrates. BPE is known to interact with gold through the pyridyl units. Figure 3A shows the SERS spectra for different concentrations of BPE in ethanol. The spectra clearly show the characteristic peaks of BPE at 1013

cm^{-1}, 1197 cm^{-1}, 1335 cm^{-1}, 1605 cm^{-1} and 1636 cm^{-1}. Raman band at 1197 cm^{-1} was used for monitoring the trace detection ability of the paper substrates. The Raman band is clearly distinguishable (SNR > 5) down to 1 nM concentration. The plot of the intensity of the 1197 cm^{-1} band vs concentration of BPE shows a monotonic increase of the intensity with concentration of BPE (Figure 3B). The SERS substrates exhibit excellent homogeneity with relative standard deviation of ~15%, which is close to the values observed for commercially available microfabricated SERS substrates.[41] This level of homogeneity is remarkable considering the simplicity of the fabrication approach and inherent heterogeneity of the paper substrates. In fact, the variation in the SERS signals was found to be largely due to the focal variations of the incident laser on the paper substrates as described below.

One of the important considerations in the fabrication of paper based SERS substrates is the effect of the exposure time of the paper substrates to the metal nanostructure solution. The extinction spectra of the paper substrates exposed to gold nanorod solution for different amounts of time show that the intensity of both transverse and longitudinal plasmon bands increase with the exposure time, indicating the progressive increase in the density of the nanorods adsorbed on the paper surface (Figure 4). It was also noted that the paper substrates progressively become darker overtime with adsorption of nanorods. SERS intensity of the paper substrates exposed to AuNR solution for different amount of time increased rapidly for the first 10-15 hours, followed by a small increase for subsequent exposure (Figure 4). This trend closely agrees with the intensity variation of the extinction spectra obtained from the paper substrates exposed to AuNR solution for different durations. The number of nanorods adsorbed on the paper substrates rapidly increases for the first 10-15 hours followed by a saturation of the density of the adsorbed nanorods subsequently.

One of the distinct advantages of the paper based SERS substrate is the ability to collect trace amount of analytes from real-world surfaces by swabbing across the surface. We demonstrate this unique ability of the paper substrates by swabbing a slightly wetted (in ethanol) paper on surface of a glass with trace quantities of analyte deposited on the surface (see Figure 5A). Figure 5B shows the Raman spectra (averaged over 6 different spots) obtained by swabbing the paper across the surface with different amounts of analyte. Again, we used the strongest Raman band at 1058 cm^{-1} to evaluate the efficiency of the SERS swab. It can be seen that the Raman bands of 1,4-BDT can be clearly distinguished down to 140 pg on the surface. Considering that the swabbing of the surface results only a fraction of the analyte to be absorbed into the paper, a detection limit on the order of few tens of picograms on the surface is truly remarkable.

CONCLUSIONS

We have demonstrated paper as a promising platform for the fabrication of a highly efficient SERS substrate for trace chemical detection. Our simple cost-effective approach of uniform adsorption of anisotropic plasmonic nanostructures onto paper matrix enabled a SERS enhancement factor of ~5×10^6, excellent homogeneity and better sample collection efficiency compared to conventional designs. The synergism of paper-based microfluidics and SERS based detection is expected to be truly transformative by opening up novel avenues in multi-analyte chemical and biological sensing. The results presented here lay groundwork for a novel plasmonic platform in the form of paper (i.e. *plasmonic paper*), which offers numerous advantages for printable microfluidic SERS/LSPR based chemical and biological sensors.
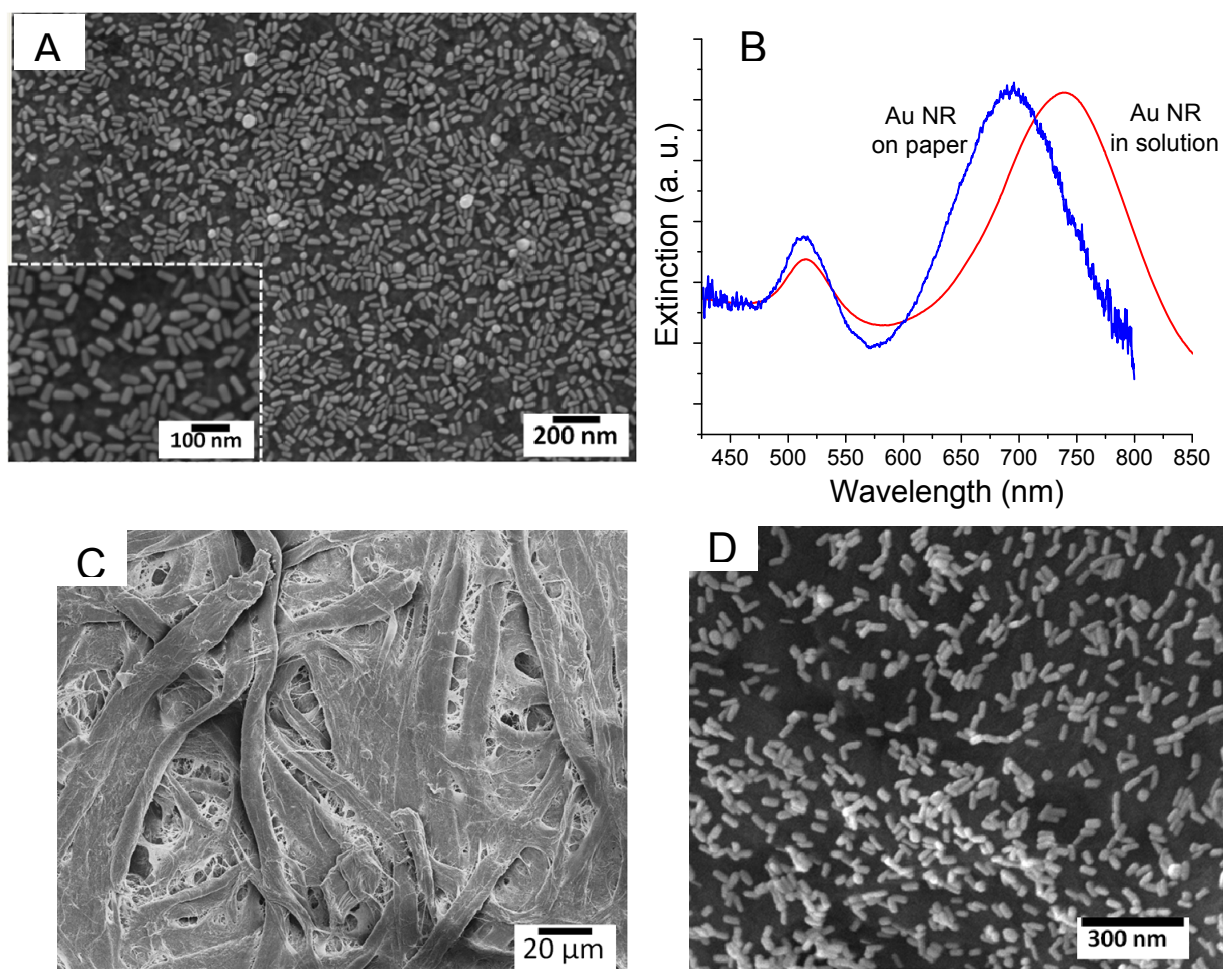
Figures

Figure 1: (A) SEM image showing AuNR adsorbed on silicon surface modified with poly(2-vinyl pyridine) (Inset shows higher magnification SEM image of gold nanorods) (B) UV-vis extinction spectra of the AuNR in solution and the same adsorbed on the filter paper. (C) SEM image of pristine paper showing the microfibers of the filter paper (D) SEM image showing the uniform decoration of the paper surface with gold nanorods.
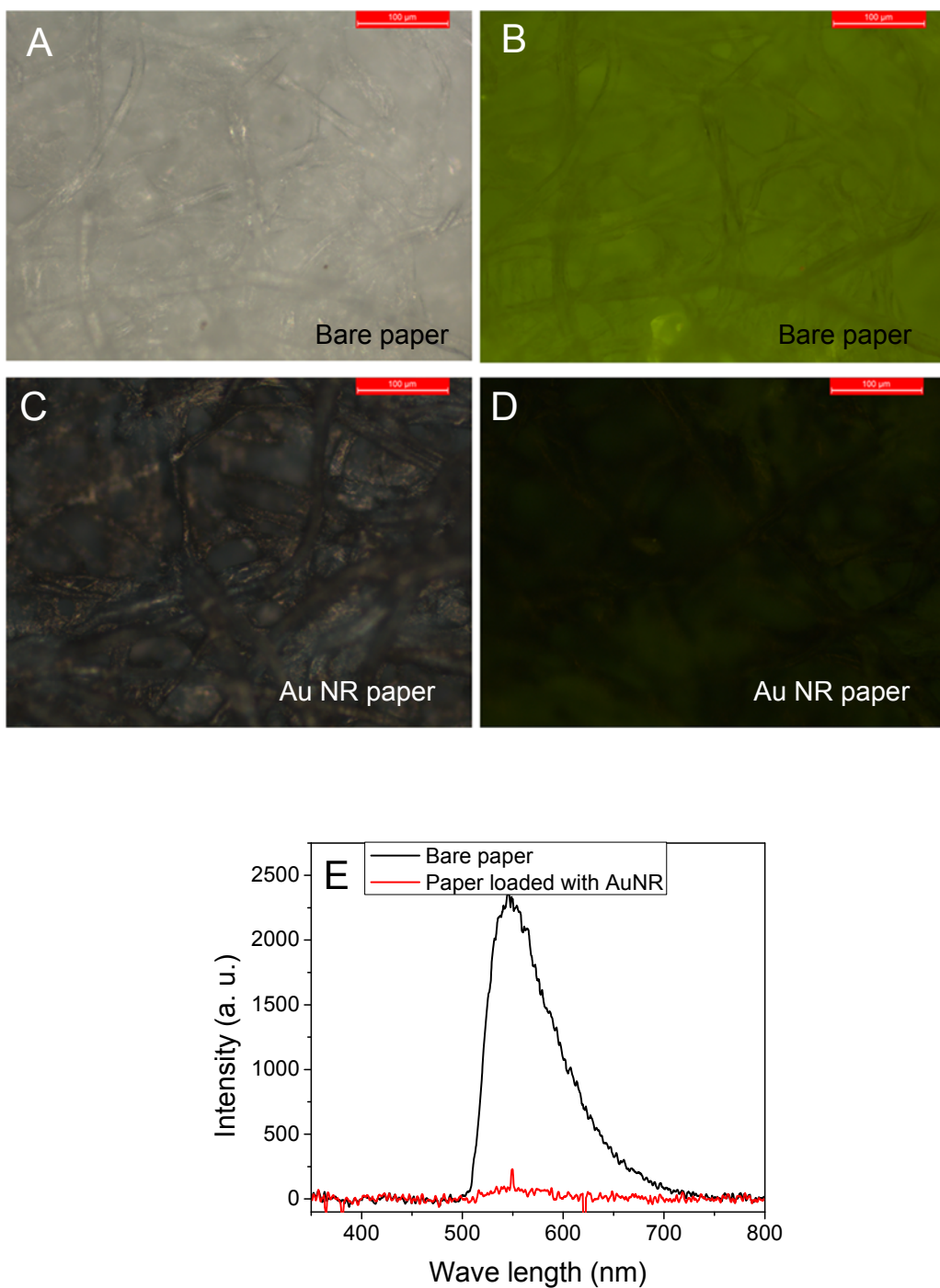
Figure 2: Bright field optical images of (A) Pristine and (C) AuNR loaded paper. Fluorescence images of (B) Pristine and (D) AuNR loaded paper. (Scale bars in all the images correspond to 100 μm) (E) Fluorescence spectra showing the quenching of the autofluorescence of the paper with adsorption of AuNR.
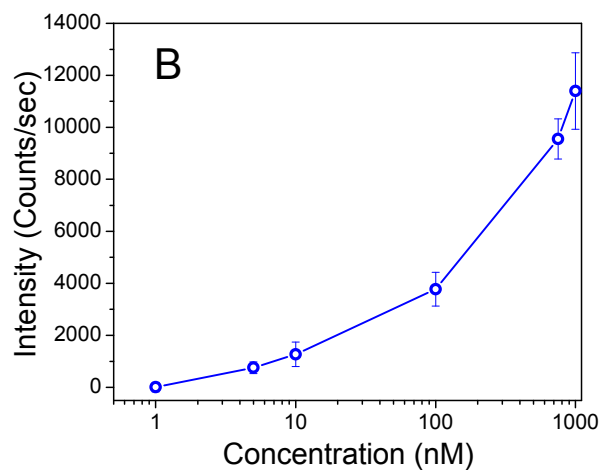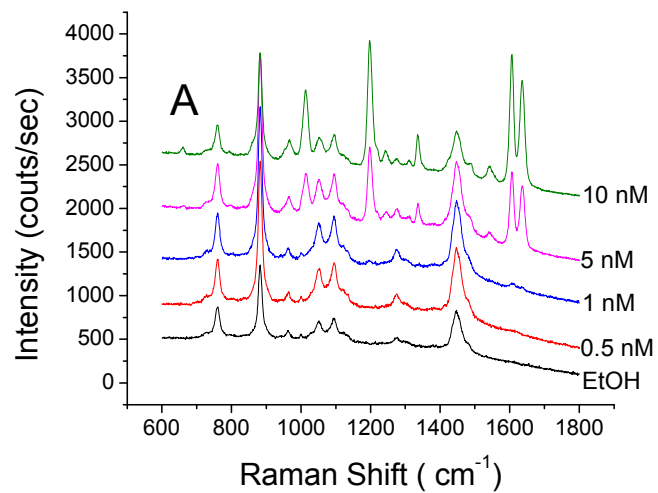
Figure 3: (A) SERS spectra obtained from the paper substrate adsorbed with nanorods as they were exposed to different concentrations BPE in ethanol. (B) Plot showing the concentration vs intensity of the 1197 cm^{-1} Raman band showing the monotonic increase of intensity with concentration of the analyte.
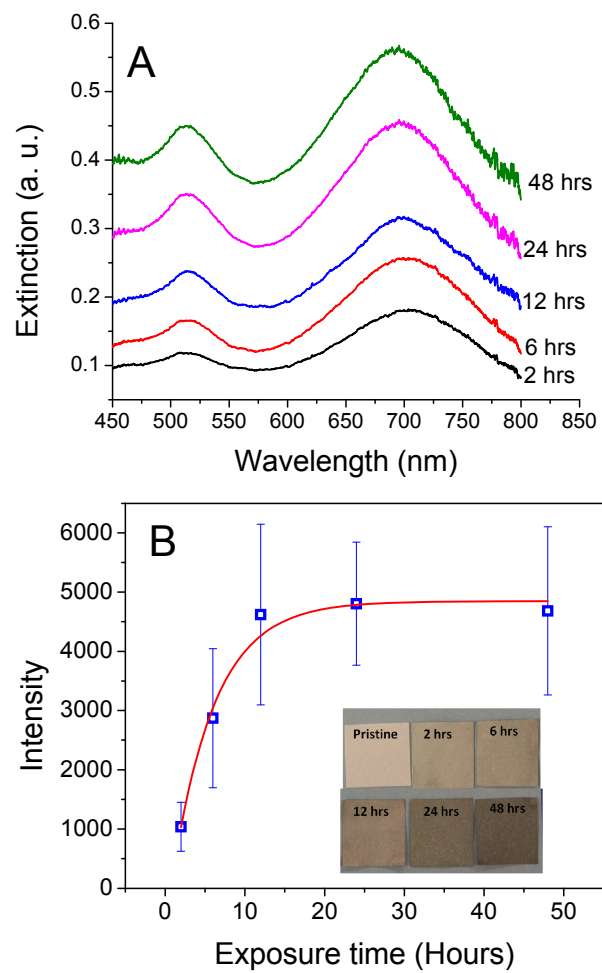
Figure 4: (A) Extinction spectra obtained from paper substrates exposed to AuNR solution for different durations (2, 6, 12, 24, 48 hrs) (B) Intensity of the SERS spectra obtained from the same substrates following the exposure to 1 mM 1,4-BDT (Inset shows the photograph of the paper substrates with progressively deepening of the color).
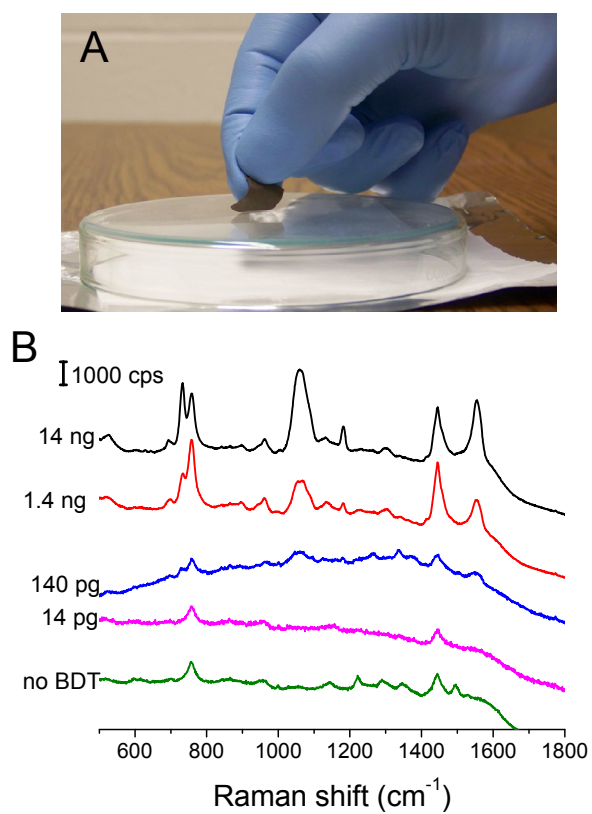
Figure 5: (A) photograph showing the SERS substrate being swabbed on the glass surface to collect trace amounts of analyte (B) SERS spectra from AuNR loaded paper swabbed on a glass surface with different amounts of 1,4-BDT.

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